DYNAMIC MODELING OF A REACTIVE DISTILLATION COLUMN

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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ABSTRACT

This research focuses on white box modeling of the dynamics of a reactive distillation column, precisely, one that is used for the commercial production of MTBE (methyl-tert-butyl-ether) by the reaction between methanol and isobutylene. The motivation for this study is mainly the process complexity posed by simultaneous reaction and separation which complicates the design and control of the column. In this study, an equilibrium model of reactive distillation column is developed in MATLAB by putting together the MESH equations and other equations like Francis weir formula and reaction rate law. Subsequently, the developed model is validated by comparison of simulation results with industrial data. Finally, the dynamic behaviour of the system is studied by applying step changes to each of the input variables, one at a time. The model of reactive distillation column is successfully developed. It is also proven to be a good representation of the column in the industry because model predictions and plant data come to a good agreement.

ABSTRAK

Kajian ini memberi tumpuan kepada pemodelan kotak putih dinamik kolum penyulingan reaktif, secara tepatnya, kolum yang digunakan untuk pengeluaran komersial MTBE (metil-tert-butil-eter) oleh tindak balas antara metanol dan isobutena. Motivasi untuk kajian ini ialah kerumitan proses yang disebabkan oleh tindak balas dan pemisahan serentak yang merumitkan perekaan dan kawalan kolum. Dalam kajian ini, model keseimbangan kolum penyulingan reaktif diterbitkan dalam MATLAB dengan mengumpulkan persamaan MESH dan persamaan lain seperti formula empang dasar Francis dan persamaan kadar tindak balas. Selepas itu, model yang diterbitkan telah disahkan melalui perbandingan keputusan simulasi dengan data industri. Akhir sekali, tingkah laku dinamik sistem dikaji dengan melakukan perubahan langkah untuk setiap pemboleh ubah dimanipulasi, satu pada satu-satu masa. Model kolum penyulingan reaktif berjaya diterbitkan. Ia juga terbukti bahawa model tersebut mampu mewakili kolum dalam industri dengan baiknya kerana keputusan simulasi dengan data industri adalah mirip.

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LIST OF SYMBOLS

r	Rate of reaction per unit mass of catalyst
q	Number of equivalent acid groups on one unit mass of catalyst
a	Activity of different components
k_f	Rate constant of the forward reaction
K_{eq}	Equilibrium constant
T	Temperature
E_n	Murphree tray efficiency
y_n	Actual vapour composition
y_{n-1}	Actual composition of vapour received from the tray below
y^*_n	Equilibrium vapour composition that corresponds to the bulk liquid composition on the tray
x_i	Initial value of variable x
y_i	Initial value of variable y
y_{i+1}	New value of variable y
h	Step size
i	Dummy that represents components
j	Dummy that represents stages
m	Dummy that represents reactions
M_j	Molar holdup on stage j
M_c	Molar holdup in condenser
M_b	Molar holdup in reboiler
V_j	Vapour flow rate from stage j
L_j	Liquid flow rate from stage j
F_j	Feed flow rate to stage j
$\sum$	Summation notation
$v_{i,m}$	Reaction coefficient of component i in reaction m
$r_{m,j}$	Rate of reaction m on stage j per unit mass of catalyst
W_j	Weight of catalyst on stage j
$z_{i,j}$	Composition of component i in feed to stage j
$x_{i,j}$	Composition of component i in liquid flow from stage j
$y_{i,j}$	Composition of component i in vapour flow from stage j

h_j	Enthalpy of liquid flow from stage *j*
H_j	Enthalpy of vapour flow from stage *j*
$h_{F,j}$	Enthalpy of liquid feed to stage *j*
$H_{F,j}$	Enthalpy of vapour feed to stage *j*
q	Degree of superheat or liquid fraction in feed
$\Delta H^R_{m,j}$	Heat of reaction of reaction *m* on stage *j*
R	Reflux flow rate
D	Distillate flow rate
Q_C	Condenser duty
B	Bottom product flow rate
Q_B	Reboiler duty
P	Pressure
γ_i	Activity Coefficient
P_i^{sat}	Vapour pressure of component *i*
l_w	Weir length
H_{ow}	Weir height
t	Time
F_L	Liquid flow rate over weir

LIST OF ABBREVIATIONS

RDC	Reactive distillation column
PID	Proportional, integral and derivative
MTBE	Methyl tert-butyl-ether
MeOH	Methanol
IB	Isobutylene
MESH	Mass balance, equilibrium relation, summation equation and heat balance
EQ	Equilibrium
NEQ	Nonequilibrium
UNIQUAC	Universal Quasichemical

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CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Reactive distillation is a process in which catalytic reactions and separation by distillation are carried out simultaneously in a column. A schematic diagram of reactive distillation column is shown in figure 1.1. Industrial applications of the process include the production or decomposition of esters, ethers and alcohols, selective hydration of olefins or aromatics and isomerization reactions (Moritz *et al.*, 2003).

Amongst the benefits of employing such operation is that the process simplification by combining reaction and separation reduces capital costs, this is because plant owners need not purchase reactors and distillation columns separately as they come in a 'package'. Next, it improves conversion for reversible reactions as the built-in separation enables product species to be taken away from the reaction zone, in this way, the system equilibrium shifts towards the right according to Le Chatelier's principle and more reactants will be consumed to form products. For the same reason, reactive distillation improves selectivity and minimizes side reactions. Finally, if the reaction taking place in the column is exothermic, heat integration benefits can be

derived because the liberated heat can be utilized for the heat of vaporization and reduce reboiler duty (Taylor and Krishna, 2000).

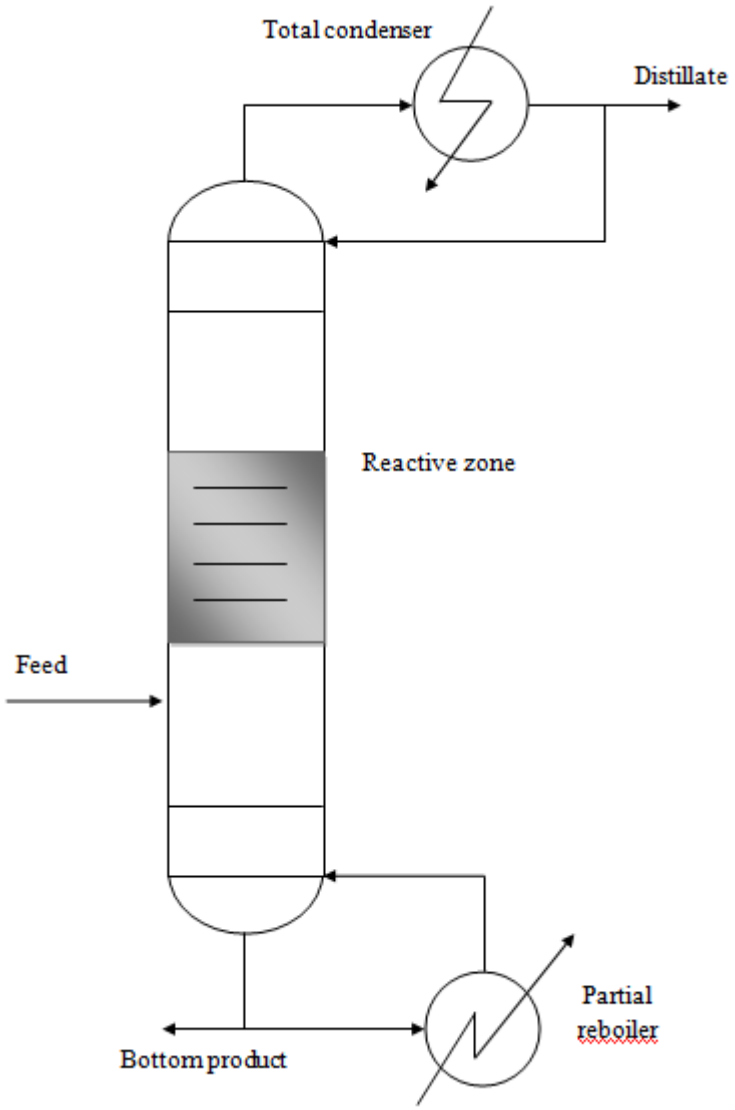

Figure 1.1: A schematic diagram of reactive distillation column

Despite having numerous advantages, reactive distillation does have some drawbacks. Firstly, it is not practical for reactions that require long residence time as a large column and tray holdup would be needed, hence it is likely more economic to

resort to the conventional reaction-followed-by-separation setup. Besides, for cases where the optimum operating conditions of reaction and distillation are far from each other, it simply defeats the purpose of the combination. Moreover, it is not suitable for large flow rates due to liquid distribution problems in packed section, too large a flow rate will cause liquid to accumulate at different parts of the packing or even flood it, this situation impedes the up bound flow of vapor and renders the entire column ineffective. Lastly, the reactants and products must have suitable volatilities, if they have similar volatilities, they would vaporize to the same extent and would not achieve a good extent of separation (Taylor and Krishna, 2000).

1.2 PROBLEM STATEMENT

The reactive distillation column is associated with complex processing configurations which complicate the design procedures and considerations. Precisely, there exists multiplicity and nonlinear interactions between reaction kinetics, intra-catalyst diffusion, vapor-liquid equilibrium and mass transfer (R. Taylor & R. Krishna, 2000). Moreover, in most chemical industries, where more often than not, products of high purity, processes of high selectivity and conversion are desired, the process nonlinearity is amplified. Distillation systems become highly nonlinear as the purity exceeds 98% (Olanrewaju and Al-Arfaj, 2005). A good dynamic model is also necessary to verify the design of the column.

Next, the dynamics and control of RDC are poorly understood as there lacks publications in the literature (Peng *et al.*, 2003). The nonlinearity of the system also poses problems to the control aspects of the reactive distillation column. Standard PID tuning with fixed parameters is inadequate for handling such processes (Bisowarno *et al.*, 2004). For complex processes such as this, advanced control strategies like model based controllers should be employed and this can only be made possible by a thorough understanding of the dynamics of the reactive distillation column. In addition, most of the published works appear to be steady-state models (Peng *et al.*, 2003).

1.3 OBJECTIVES

This research aims to attain the objectives below as part of the requirements for its success.

i. To develop an equilibrium model for reactive distillation column.

ii. To validate the model with industrial data.

iii. To study the dynamic performance of developed model.

1.4 SCOPE OF STUDY

The scope of this study is chosen in order to set the limit to where this research will explore, and also to ensure that the research objectives can be achieved without deviations. This study focuses on the white box modeling of the commercial MTBE (methyl tert-butyl ether) production by the reaction of methanol and isobutylene in a reactive distillation column.

1.5 SIGNIFICANCE OF RESEARCH

The developed process model for reactive distillation column will contribute to the following aspects (Seborg *et al.*, 2004):

i. Design of the reactive distillation column; the model allows dynamic and steady-state behavior of the system to be detailed and understood. This information will greatly ease the design.

ii. Development of control strategies; with the knowledge about the system behavior at disposal, various control methods can be proposed and tested. The effectiveness of different control strategies can be compared and the best method determined and implemented.

iii. Optimization of operating conditions; owners of the column can utilize the model to estimate the optimum operating conditions from time to time. In this way, the owner is subjected to benefits in yield, profit and rate of product manufacture.

iv. Training for plant operating personnel; the model can be developed into a simulation software to provide a realistic situation that imitates the circumstances when the reactive distillation column is to be operated. With that, plant workers can learn to operate and get familiar with the equipment before they are actually put on duty.

CHAPTER 2

LITERATURE REVIEW

2.1 MTBE

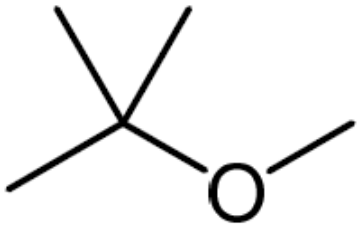

Figure 2.1: Skeletal Structure of MTBE

The above figure shows the skeletal structure of MTBE (or methyl tert-butyl ether in full). MTBE is an organic compound with molecular formula $C_4H_9OCH_3$ and a molecular weight of 88.15 g/mol. It is a colourless liquid with an ether-like smell and is extremely volatile and flammable. It is widely used around the globe as a gasoline oxygenate to increase the octane number. High purity MTBE is utilized as a solvent in labs as well as pharmaceutical industries (Hatermann, n.d.)

2.2 REACTION KINETICS

The reversible reaction between methanol (MeOH) and isobutylene (IB) to produce MTBE can be represented by the following equation:

$$MeOH + IB \leftrightarrow MTBE \tag{2.1}$$

The reaction is heterogeneously catalyzed by Amberlyst 15. The rate of the liquid phase reaction can be described by the rate equation as shown below (Rehfinger and Hoffmann, 2001; Eldarsi and Douglas, 1998):

$$r = qk_f \left(\frac{a_{IB}}{a_{MeOH}} - \frac{a_{MT\,BE}}{K_{eq}\, a_{MeOH}^2}\right) mol/s\,.\,kg \tag{2.2}$$

r represents the rate of reaction per unit mass of catalyst while q is the number of equivalent acid groups on one unit mass of catalyst resin (4.9 equiv/kg for Amberlyst 15), a is the activity of different components, k_f is the rate constant of the forward reaction, K_{eq} is the equilibrium constant. The expressions for k_f and K_{eq} are as follows:

$$k_f = 3.67 \times 10^{12} \exp\left(\frac{-11110}{T}\right) mol/s\,.\,kg \tag{2.3}$$

$$K_{eq} = 284 \exp[f(t)] \tag{2.4}$$

$$f(t) = A_1\left(\frac{1}{T} - \frac{1}{T_0}\right) + A_2 \log\left(\frac{T}{T_0}\right) + A_3(T - T_0) + A_4(T^2 - T_0^2) + A_5(T^3 - T_0^3) + A_6(T^4 - T_o^4) \tag{2.5}$$

where

$T_o = 298.15\ K$

$A_1 = -1.49277 \times 10^3\ K$

$A_2 = -77.4002$

$A_3 = 0.507563\ K^{-1}$

$A_4 = -9.12739 \times 10^{-4}\ K^{-2}$

$A_5 = 1.10649 \times 10^{-6}\ K^{-3}$

$A_6 = -6.27996 \times 10^{-10}\ K^{-4}$

2.3 TYPES OF MATHEMATICAL MODELS

2.3.1 White Box Model

A white box model is a list of equations that represents a system or process; it is developed from theories of science, namely, conservation principles that apply to mass, energy and momentum as well as relations that govern the equilibrium between liquid and vapor. What differentiates a white box model from the other types is that it provides details about the insights of a system (Seborg *et al.*, 2004). The followings are equations that constitute a white box model of a reactive distillation column:

$$\frac{dU_j}{dt} = V_{j+1} + L_{j-1} + F_j - (1 + r_j^V)V_j - (1 + r_j^L)L_j + \sum_{m=1}^{r}\sum_{i=1}^{c} v_{i,m}R_{m,j}\varepsilon_j$$

$$y_{i,j} = K_{i,j}x_{i,j}$$

$$\sum_{i=1}^{c} x_{i,j} = 1, \quad \sum_{i=1}^{c} y_{i,j} = 1$$

$$\frac{dU_j x_{i,j}}{dt} = V_{j+1}y_{i,j+1} + L_{j-1}x_{i,j-1} + F_j z_{i,j} - (1 + r_j^V)V_j y_{i,j} - (1 + r_j^L)L_j x_{i,j} + \sum_{m=1}^{r} v_{i,m}R_{m,j}\varepsilon_j$$

$$\frac{dU_j H_j}{dt} = V_{j+1}H_{j+1}^V + L_{j-1}H_{j-1}^L + F_j H_j^F - (1 + r_j^V)V_j H_j^V - (1 + r_j^L)L_j H_j^L - Q_j$$

Figure 2.2: An example of white box model

Source: Taylor and Krishna (2000)

2.3.2 Black Box Model

Unlike in a white box model, the system under consideration is treated like an opaque box, that is, only the input and output for the system are considered but the inner workings are not known. The development of a black box model is based on regression to find the relations between the input and output (Seborg *et al.*, 2004). A black box model which represents the temperature increase due to heat liberation by thermogenin, a mitochondrial membrane protein is shown below:

$$\dot{N} = Nr(1-\frac{N}{K})$$

$$\dot{G} = -\beta_1 N$$

$$\dot{H} = \alpha \frac{\left(\frac{G}{K_1}\right)^n}{1+\left(\frac{G}{K_1}\right)^n} - \beta_2 H + \gamma$$

$$\dot{T} = -k(T-T_a) + \xi H$$

Figure 2.3: An example of black box model

Source: IGEM (2008)

2.3.3 Grey Box Model

In a grey box or hybrid model, fundamental principles from a white box model is combined into a black box model, hence it gives better physical meaning than a complete black box model. In this approach, the model is defined partly by physical knowledge while the remaining unknown parts are described by a black box model. An example of a grey box model representing a reactive distillation column is as follows:

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} S_1 \\ S_2 \\ A \\ D \\ E \\ G \end{pmatrix} = \begin{bmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 2 & 1 & -1 & -1 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 1 & -1 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{pmatrix} r_1 \\ r_2 \\ r_3 \\ r_4 \end{pmatrix}$$

$$+\frac{1}{V}\begin{pmatrix} F_{S1,in} & S_{1,in} & -F_l S_1 \\ F_{S2,in} & S_{2,in} & -F_l S_2 \\ & & -F_l A \\ F_{D,in} & D_{in} & -F_l D \\ & & -F_l E \\ & & -F_l G \end{pmatrix} - \frac{F_v}{V}\begin{pmatrix} 0 \\ 0 \\ 0 \\ f_D \\ f_E \\ f_G \end{pmatrix} \quad \dot{Y} = -\frac{F_l}{V}Y + \frac{F_{D,in}D_{in}}{V}(U-1)$$

$$-r_4 + \frac{F_v}{V}f_D - \frac{1}{V}(F_l S_2 - F_l D)$$

Figure 2.4: An example of grey box model

Source: Chen *et al.* (2004)

2.4 DEVELOPMENT OF EQUILIBRIUM MODEL

The schematic diagram of an equilibrium stage in a reactive distillation column is shown below:

2.5 INCORPORATION OF TRAY EFFICIENCIES INTO EQUILIBRIUM MODEL

Some equilibrium models incorporate tray efficiency factors in the phase equilibrium equations as a modification (Taylor and Krishna, 2000). Ramesh K. *et al.* (2005) incorporated Murphree vapour phase efficiencies to account for departure from equilibrium between the vapour and liquid streams leaving a stage. The Murphree efficiency of tray *n* for component *j* can be calculated with the formula:

$$E_{n,j} = \frac{y_{n,j} - y_{n-1,j}}{y^*_{nj} - y_{n-1,j}} \tag{2.5}$$

where $y_{n,j}$ represents actual vapour composition, $y_{n-1,j}$ is actual composition of vapour received from the tray below while $y^*_{n,j}$ is the equilibrium vapour composition that corresponds to the bulk liquid composition on the tray. $y^*_{n,j}$ can be determined by conducting bubble point calculations.

2.6 VALIDATION OF MODEL WITH EXPERIMENTAL/INDUSTRIAL DATA

Bhatia *et al.* (2007) developed two types of models for simulation of a catalytic distillation column that produces isopropyl palmitate, they were equilibrium model and rate-based model. Subsequently, the models were used to predict the conversion of palmitic acid and liquid composition for comparison with experimental data. It was shown that the results obtained from the rate-based model were in good agreement with the experimental data. On the other hand, the equilibrium model could only describe the column behaviour qualitatively.